

Atmospheric Deposition: Acidity and Nutrients

Background

Atmospheric deposition refers to substances that are deposited on land or water surfaces from the air. These substances can be carried in precipitation, also called wet deposition, or they can reach the earth's surface via dry deposition, which includes both the settling out of particles and the adsorption by soil, trees, water or other surfaces of gaseous substances.

An important category of atmospheric deposition is acidity. In precipitation, most acidity is contributed by sulfuric acid (H_2SO_4) and nitric acid (HNO_3). Deposition of associated nutrients, especially nitrate (NO_3^-) and sulfate (SO_4^{2-}), has important impacts on the environment. Nitrate deposition especially can cause eutrophication of coastal and other water bodies and damage to terrestrial ecosystems. Terrestrial ecosystems encompass ground-based ecosystems such as forests. Nitrate is harmful to terrestrial ecosystems because it can harm beneficial fungi and may encourage the growth of invasive species. Nitrate^{1,2,3} is the subject of current DEP research.⁴ Sulfate can combine with calcium and other nutrients necessary for plant growth, causing them to leach more quickly from the soil.

Sulfuric and nitric acids are present in unpolluted precipitation at low levels. However, in much of the eastern U.S., due to anthropogenic emissions of SO_2 and NO_x , the concentrations of these acids in precipitation are so high that the pH of rain is often in the 3.5 to 5.0 range.⁵ Some fogs have been measured with pH readings as low as 2.0, which is highly acidic.⁶ Most of the SO_2 comes from coal-burning power plants, whereas NO_x comes from a variety of combustion sources including power plants, other industrial facilities, area sources (including commercial and residential buildings) and motor vehicles.

Acid precipitation has damaged wildlife and ecosystems in many parts of the United States and Europe. Regions where the soils and water bodies have limited buffering capacity, or the ability to neutralize the deposited acids, have been affected the most. The buffering capacity of most soils is sufficient to neutralize naturally occurring acids, but over time the capacity can be overwhelmed by high inputs of acid deposition. A dramatic effect of the acidification of some water bodies is loss of fish species, which has happened in areas such as the Adirondack region of New York.

Ecosystem effects of acid rain are widespread. Studies at Hubbard Brook Experimental Forest in New Hampshire have revealed that concentrations

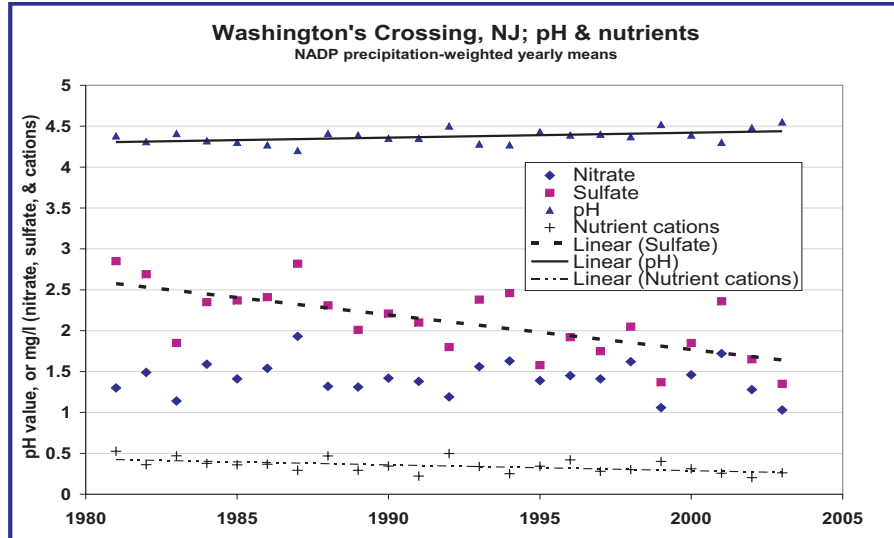
of the nutrients calcium and magnesium (which neutralize acidity, but are leached from soils in the process) have been lowered and vegetative growth has slowed as a result of decades of acidic precipitation. Studies at other sites in the Northeast also show reductions in nutrient levels as well as the release of aluminum, which can block nutrient uptake by vegetation. Acid fogs and rains also have been found to leach calcium directly from spruce needles, damaging the trees.⁷

Status and Trends

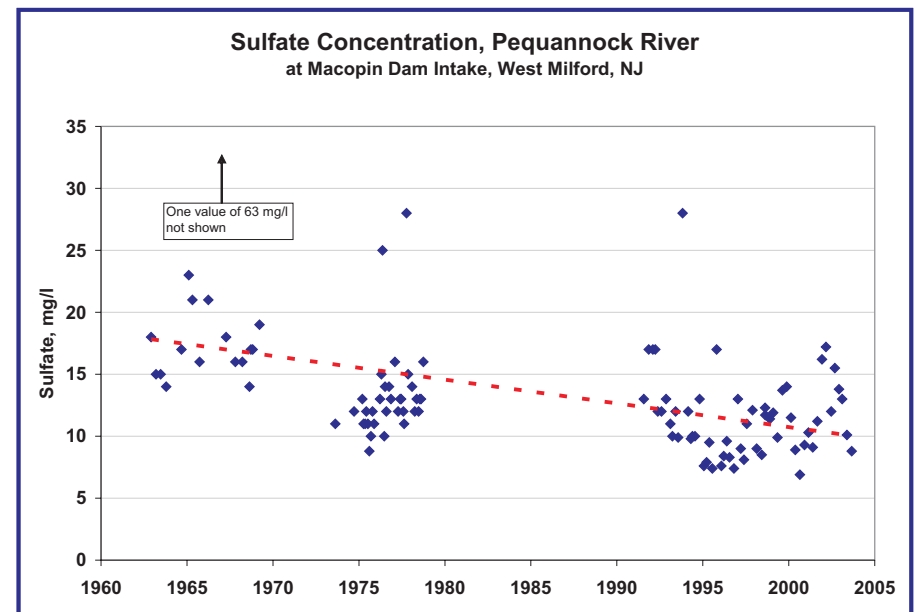
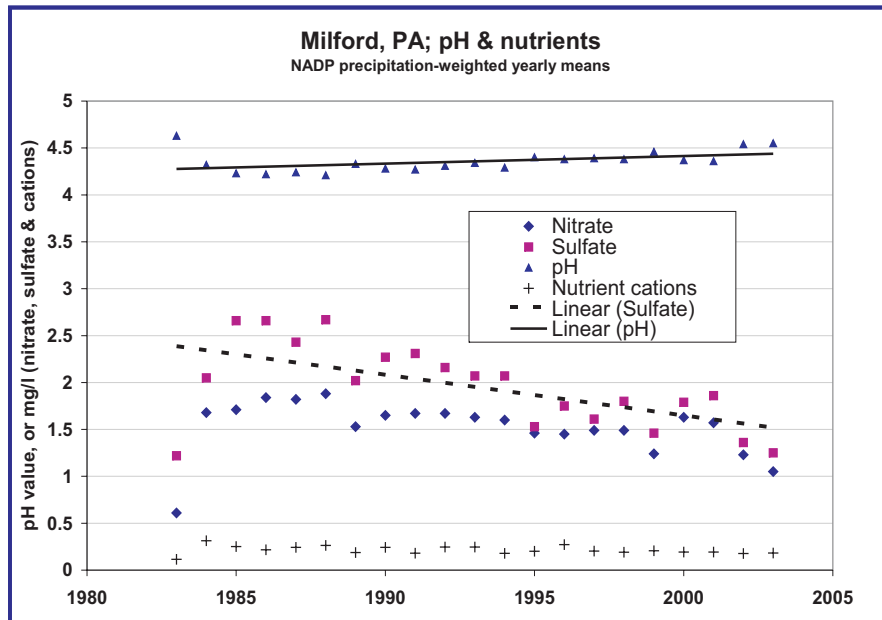
New Jersey has two sites that are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), a nationwide network of precipitation monitoring sites, where acid precipitation and nutrients are measured. The network is a cooperative effort between many different groups, including state agricultural experiment stations, U.S. Geological Survey, U.S. Department of Agriculture, and numerous other governmental and private entities, including DEP. The purpose of the network is to collect data on the chemistry of precipitation for monitoring of geographical and temporal long-term trends. The precipitation at each station is collected weekly and then analyzed at a central laboratory.⁸

The DEP monitors acid precipitation at two additional sites, Lebanon State Forest and Ancora State Hospital, and dry deposition of particles at three sites – Fort Lee, Elizabeth and Camden.⁹ Further, deposition of nitrate has been measured at New Brunswick, Camden, the Pinelands and Jersey City through the New Jersey Atmospheric Deposition Network (NJADN) for a multiyear study of atmospheric deposition of a number of contaminants.¹⁰ Data collected at all New Jersey sites generally are consistent with NADP/NTN data and show similar deposition patterns at all sites.

Long time series of data on acidity and nutrients in precipitation in the vicinity of New Jersey area are available for the NADP/NTN sites at Washington's Crossing, NJ and Milford, PA (just west of northern NJ). (See the charts Washington's Crossing, NJ; pH & nutrients, and Milford, PA; pH & nutrients, on the next page).



These data show a significant decline in deposition of sulfate and nutrient cations and a significant increase in pH. The average pH of precipitation is in the range of 4.5, which is still 10 times more acidic than expected for unpolluted rain in the Northeast. The decline in deposition of nutrient cations¹¹ likely reflects increased control of emissions of particles, which can include cations, from combustion sources.



Reductions of sulfate in precipitation are also reflected in lower sulfate concentrations of some surface waters, for example the Pequannock River, near West Milford, NJ. See chart, Sulfate Concentration, Pequannock River, which shows a significant decline in sulfate concentration over time in that river.

Outlook and Implications

Rules are in place at both federal and state level to reduce emissions of SO₂ and NO_x from sources such as industrial facilities.¹² Some of these rules have been in effect for more than two decades and have reduced U.S. emissions of SO₂ by about 40 percent.^{13,14} Studies have shown a virtually universal reduction in deposition of sulfates because of a decrease in SO₂ emissions, but there has not been a decrease in overall acidity in many regions.¹⁵ The data in the chart, Washington's Crossing, NJ; pH and nutrients, are consistent with these studies, showing a significant drop in sulfate deposition, but only a modest change in pH. The limited change in pH level may be due to in part to a decrease in deposition of nutrient cations, which increase pH by buffering acidity.

Despite a general decline in acid deposition in both Europe and North America, some areas show significant delay in aquatic recovery from acidification, and minimal biological recovery in waters or soils.¹⁶ This delay probably is due to a depletion of neutralizing substances in soils and water bodies due to years of impact from acidic deposition. New, more stringent controls on NO_x emissions recently have been implemented at the federal level and in New Jersey,¹⁷ and these reductions are expected to have a positive impact on acidic deposition and nitrate deposition. Whether these additional reductions will be sufficient to offset long-term impacts on some ecosystems still is unclear. In some affected areas, it is estimated that an additional 80 percent reduction in emissions of SO₂ and NO_x will be required to permit soils to regenerate the base cation levels needed for healthy trees.¹⁸

More Information

See the DEP Bureau of Air Monitoring Web site, www.state.nj.us/dep/airmon/, and the EPA acid rain program Web site www.epa.gov/airmarkets/arp/

References

- ¹ Pelley, Janet, 1998, Is Coastal Eutrophication Out of Control?, *Env. Sci. Technol.* Oct. 1, 1998, 462A-466A.
- ² Seitzinger, Sybil, M. Mazurek, R. Styles, and R. Lauck, 2000, Atmospheric Deposition of Nitrogen to Coastal Ecosystems, presentation to NJDEP by Seitzinger, Sybil, et al., Institute of Marine & Coastal Sciences, Rutgers University.
- ³ Castro, Mark and Charles Driscoll, 2002, Atmospheric nitrogen deposition to estuaries in the Mid-Atlantic and Northeastern U.S., *Env. Sci. Technol.* 36, 3242-3249.
- ⁴ NJDEP, 2005, Assessing Impacts of Atmospheric Nitrogen

Deposition on New Jersey Forests 2002-2003 - Final Report Year 1, available at <http://www.state.nj.us/dep/dsr/wq/dep-njforests.htm>.

⁵ The pH is the antilog of the concentration of hydrogen ions, H⁺, in moles per liter. Thus a sample with a pH of 5.0 has 1 x 10⁻⁵ moles of H⁺ per liter. Rainfall, unless buffered by cations in airborne particles, tends to be naturally acidic, with a pH in the range of 5.6. This is due to the presence in the air of carbon dioxide, which dissolves in water producing carbonic acid.

⁶ Spiro, Thomas, and William Stigliani, 2003, *Chemistry of the Environment*, 2nd Edition, Prentice Hall, Upper Saddle River, NJ 07458, page 279.

⁷ Spiro & Stigliani, 2003, p. 301.

⁸ See the National Atmospheric Deposition Program web site at <http://nadp.sws.uiuc.edu/>.

⁹ NJDEP, 2005, 2001 Acid Deposition Summary, 2001 Air Quality Report, available from <http://www.state.nj.us/dep/airmon/reports.htm>

¹⁰ Reinfelder, John, Lisa Totten, and Steven Eisenreich, 2004, The New Jersey Atmospheric Deposition Network, Final Report to the NJDEP, Michael Aucott, project manager, May, 2004.

¹¹ "Nutrient cations" in this case represents the sum of the yearly precipitation-weighted mean concentrations of calcium, magnesium, potassium, and phosphorus ions.

¹² For relevant NJ rules, see <http://www.state.nj.us/dep/aqm/rules.html#27>. Also see the USEPA acid rain program web site at <http://www.epa.gov/airmarkets/arp/>.

¹³ Spiro & Stigliani, 2003, p. 303.

¹⁴ Rules are in place in Europe as well, although they are not based on a cap and trade program as in the U.S. The European rules have led to a similar, perhaps even relatively larger, reduction in emissions.

¹⁵ Yoon, Carol K., 1999, Report on acid rain finds good news and bad news: sulfate levels drop, but acidity continues, *NY Times*, October 7, 1999.

¹⁶ Alewell, C., B. Manderscheid, H. Meesenburg, and J. Bittersohl, 2000, Is acidification still an ecological threat, *Nature*, 407, 856-857.

¹⁷ Title IV of the Clean Air Act set a goal of reducing annual SO₂ emissions by 10 million tons below 1980 levels. This was to be achieved in two phases. Emissions data indicate that 1995 SO₂ emissions at regulated units nationwide were reduced by almost 40% below their required level. Phase II, which began in the year 2000, tightened the annual emissions limits imposed on these large, higher emitting plants and also set restrictions on smaller, cleaner plants fired by coal, oil, and gas, encompassing over 2,000 units in all. The Act also called for a 2 million ton reduction in NO_x emissions by the year 2000. A significant portion of this reduction has been achieved by coal-fired utility boilers that will be required to install low NO_x burner technologies and to meet new emissions standards. See the USEPA acid rain program web site at <http://www.epa.gov/airmarkets/arp/overview.html#phases> and also the NJDEP Air Quality Permitting Program web site at <http://www.nj.gov/dep/aqpp/>

¹⁸ Spiro & Stigliani, 2003, p. 303.